

# Carbonylation

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**Carbonylation** refers to reactions that introduce carbon monoxide into organic and inorganic substrates. Carbon monoxide is abundantly available and conveniently reactive, so it is widely used as a reactant in industrial chemistry.

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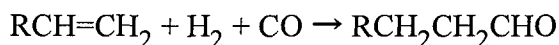
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## Organic chemistry

Several chemicals used significantly in industry are prepared by carbonylation, which can be highly selective reactions. Carbonylations produce organic carbonyls, i.e., compounds that contain the C=O functional group.<sup>[1][2]</sup> Carbonylations are the basis of two main types of reactions, *hydroformylation* and *Reppe Chemistry*.

### Hydroformylation

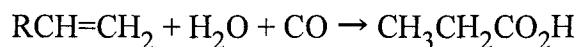
Hydroformylation entails the addition of both carbon monoxide and hydrogen to unsaturated organic compounds, usually alkenes. The usual products are aldehydes:



The reaction requires metal catalysts that binds the CO, the H<sub>2</sub>, and the alkene, allowing these substrates to combine within its coordination sphere.

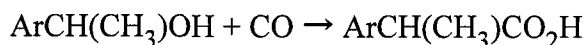
### Reppe Chemistry

Reppe Chemistry, named after Walter Reppe, entails addition of carbon monoxide and an acidic hydrogen donor to the organic substrate. The largest-scale application of this type of carbonylation is the Monsanto acetic acid process, which produces acetic acid from methanol. Acetic anhydride is prepared by a related carbonylation of methyl acetate.<sup>[3]</sup> In the related hydrocarboxylation and hydroesterification, alkenes and alkynes are the substrates. This method is used in industry to produce propionic acid from ethylene:



These reactions require metal catalysts, which bind and activate the CO. In the industrial synthesis of

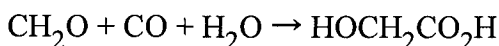
Ibuprofen, a benzylic alcohol is converted to the corresponding carboxylic acid via a Pd-catalyzed carbonylation:<sup>[1]</sup>



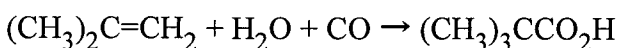
Acrylic acid was once prepared by the hydrocarboxylation of acetylene but is now produced by the oxidation of propene.

## Other reactions

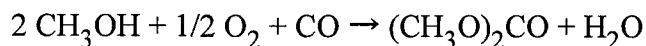
The Koch reaction (also the related Koch-Haaf reactions) entail the addition of CO to unsaturated compounds in the presence of strong acids such as sulfuric acid. This method is less frequently used in industry as are the metal-catalyzed reactions, described above. The industrial synthesis of glycolic acid is achieved in this way:<sup>[4]</sup>



The conversion of isobutene to pivalic acid is also illustrative:



Unrelated to the Koch reaction, dimethylcarbonate and dimethyloxalate are also produced in industry from carbon monoxide.<sup>[1]</sup> These reactions require oxidants:



## Inorganic chemistry

[[Metal carbonyls, compounds with the formula  $\text{M}(\text{CO})_n\text{L}_x$  (M = metal,  $\text{L}_x$  = a variety of ligands) are prepared by carbonylation of transition metal. Iron and nickel powder react directly with CO to give  $\text{Fe}(\text{CO})_5$  and  $\text{Ni}(\text{CO})_4$ , respectively. Most other metals form carbonyls less directly, such as from their oxides or halides. Metal carbonyls widely employed as catalysts in the hydroformylation and Reppe processes discussed above.<sup>[5]</sup>

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# Hydrocyanation

From Wikipedia, the free encyclopedia

**Hydrocyanation** is, most fundamentally, the process whereby  $\text{H}^+$  and  $\text{CN}^-$  ions are added to a molecular substrate. Usually the substrate is an alkene and the product is a nitrile. When  $\text{CN}^-$  is a ligand in a transition metal complex, its basicity makes it difficult to dislodge, so, in this respect, hydrocyanation is remarkable. Since cyanide is both a good  $\sigma$ -donor and  $\pi$ -acceptor its presence accelerates the rate of substitution of ligands *trans* from itself, the *trans* effect.<sup>[1]</sup> A key step in hydrocyanation is the oxidative addition of hydrogen cyanide to low-valent metal complexes.<sup>[1]</sup>

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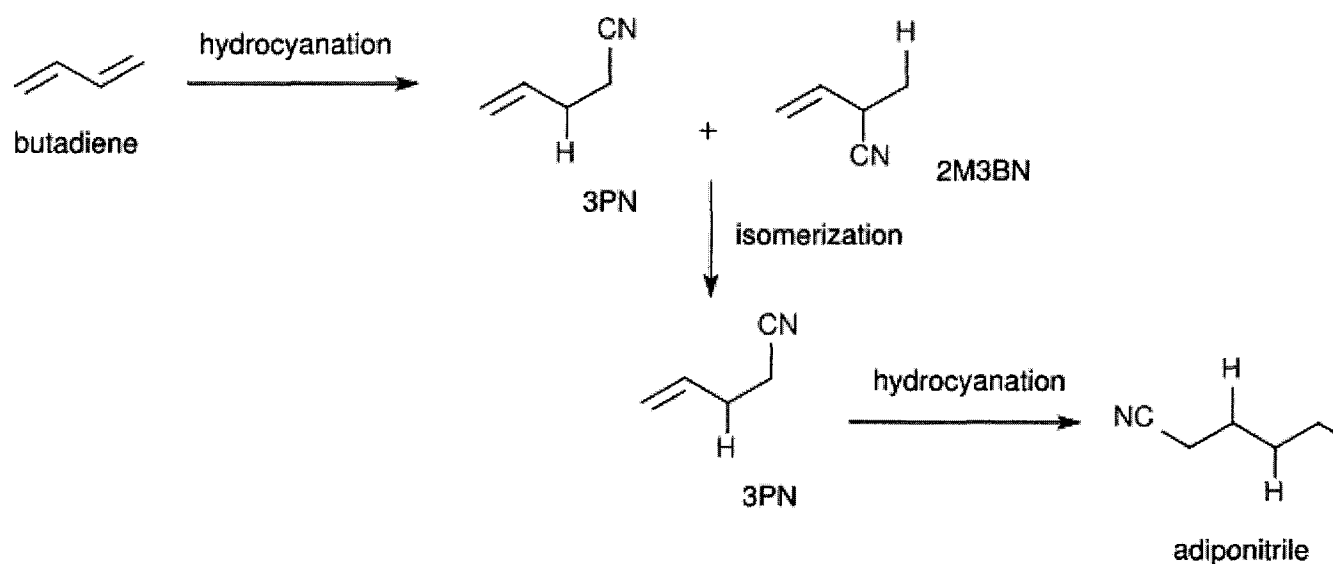
## Inorganic Chemistry

Hydrocyanation is performed on alkenes and alkynes with copper, palladium, and most commonly, nickel catalysts.<sup>[1]</sup> Industrial hydrocyanation utilizes phosphite ( $\text{P(OR)}_3$ ) complexes of nickel. Phosphites give excellent catalysts, whereas the related phosphine ( $\text{PR}_3$ ) ligands, which are more basic, are catalytically inactive.<sup>[1]</sup> Chiral, chelating aryl diphosphite complexes are commonly employed in asymmetric hydrocyanation. An example of a nickel-phosphite catalyzed hydrocyanation of ethene<sup>[1]</sup>.

Lewis acids, such as  $\text{B(C}_6\text{H}_5)_3$ , can increase hydrocyanation rates and allow for lower operating temperatures.<sup>[2]</sup> Triphenylboron may derive this ability from sterically protecting the  $\text{CN}^-$  as it is bound to nitrogen.<sup>[1]</sup> Rates can also be amplified with electron-withdrawing groups ( $\text{NO}_2$ ,  $\text{CF}_3$ ,  $\text{CN}$ ,  $\text{C(=O)OR}$ ,  $\text{C(=O)R}$ ) on the phosphite ligands, because they stabilize  $\text{Ni(0)}$ .<sup>[3]</sup> A major problem when using nickel catalysts for hydrocyanation is the production of  $\text{Ni}^0(\text{CN})_x$  as a result of excess  $\text{HCN}$ .<sup>3</sup> Bulky ligands impede the formation of these unreactive  $\text{Ni}^0(\text{CN})_x$  complexes.<sup>[4]</sup>

## Usage

Hydrocyanation is important due to the versatility of alkyl nitriles ( $\text{RCN}$ ), which are important intermediates for the syntheses of amides, amines, carboxylic acids, and ester compounds.<sup>[5]</sup> The most popular industrial usage of nickel-catalyzed hydrocyanation is for adiponitrile ( $\text{NC-(CH}_2)_4\text{-CN}$ ) synthesis from 1,3-butadiene ( $\text{CH}_2=\text{CH-CH=CH}_2$ ). Adiponitrile is a precursor to hexamethylenediamine ( $\text{H}_2\text{N-(CH}_2)_6\text{-NH}_2$ ), which is used for the production of certain kinds of Nylon. The DuPont ADN process to give adiponitrile is shown below:



This process consists of three steps: hydrocyanation of butadiene to a mixture of 2-methyl-3-butenitrile (2M3BN) and 3-pentenitrile (3PN), an isomerization step from 2M3BN (not desired) to 3PN and a second hydrocyanation (aided by a Lewis acid cocatalyst such as aluminium trichloride) to adiponitrile. [6]

Naproxen, an anti-inflammatory drug, utilizes an asymmetric enantioselective hydrocyanation of vinyl naphthalene from a phosphinite(OPR<sub>2</sub>) ligand, **L**. The enantioselectivity of this reaction is important because only the S enantiomer is medically desirable, whereas the R enantiomer produces harmful health effects. This reaction can produce the S enantiomer with > 90% selectivity. Upon recrystallization of the crude product, the optically pure nitrile can be attained.

## History

Hydrocyanation was first reported by Arthur and Pratt in 1954, when they homogeneously catalyzed the hydrocyanation of linear alkenes. [7]

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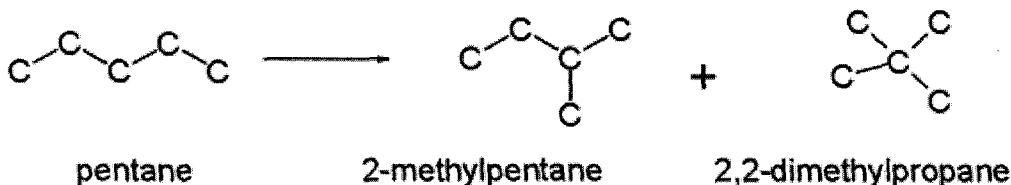
# Isomerisation

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(Redirected from Isomerization)

In chemistry, **isomerization** or **isomerisation** is the transformation of a molecule into a different isomer <sup>[1]</sup>. In some molecules and under some conditions, isomerisation occurs spontaneously. Many isomers are equal or roughly equal in bond energy, and so they interconvert relatively freely. When the isomerisation occurs intramolecularly it is considered a rearrangement reaction.

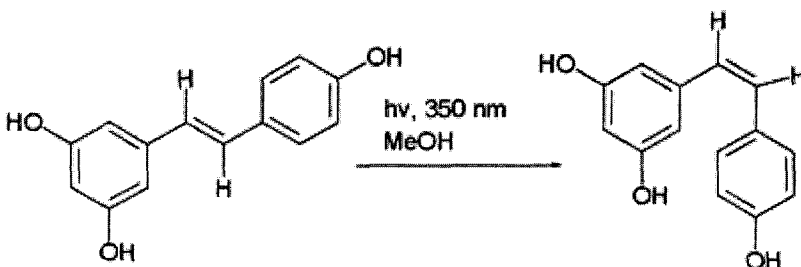
## Instances of Isomerization

- Isomerisations in hydrocarbon cracking. This is usually employed in organic chemistry, where fuels, such as pentane, a straight-chain isomer, are heated in the presence of a platinum catalyst (*see image*). The resulting mixture of straight- and branched-chain isomers then have to be separated. An industrial process is also the isomerisation of n-butane into isobutane.



Nota Bene: the first product should be 2-methylbutane, rather than 2-methylpentane.

- Trans-cis isomerism.** In certain compounds an interconversion of cis and trans isomers can be observed, for instance, with maleic acid and with azobenzene often by photoisomerization. An example is the photochemical conversion of the trans isomer to the cis isomer of resveratrol <sup>[2]</sup>:



- Aldose-ketose isomerism in biochemistry.
- Isomerisations between conformational isomers. These take place without an actual rearrangement for instance inconversion of two cyclohexane conformations
- Fluxional molecules display rapid interconversion of isomers.

The energy difference between two isomers is called **isomerisation energy**. Isomerisations with low energy difference both experimental and computational (in parentheses) are endothermic trans-cis isomerisation of 2-butene with 2.6 (1.2) kcal/mol, cracking of isopentane to n-pentane with 3.6 (4.0) kcal/mol or conversion of trans-2-butene to 1-butene with 2.6 (2.4) kcal/mol.<sup>[3]</sup>

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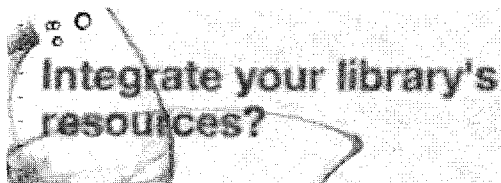


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## Amidocarbonylation of alkenes at very low pressures with a $\text{Co}_2(\text{CO})_8/\text{SbR}_3$ system: two easy routes to reach *N*-acetyl--aminoacids

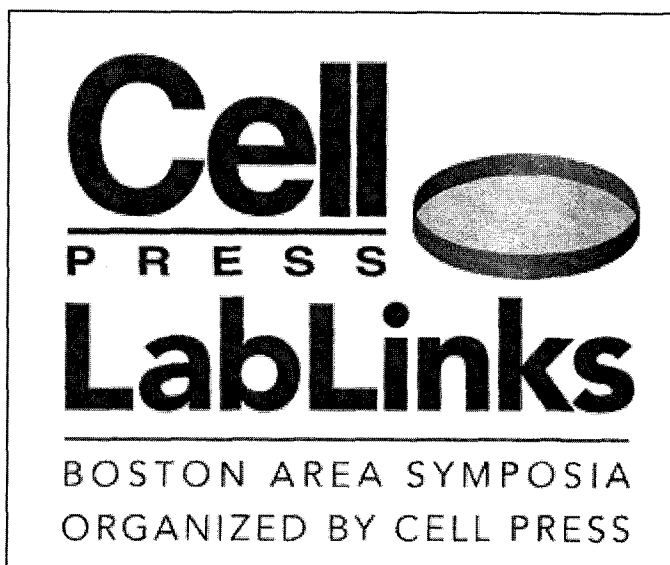
Armando Cabrera , Pankaj Sharma , José Luis Arias , José Luis Velasco , Javier Pérez-Flores and Rosa María Gómez

Instituto de Química, Universidad Nacional Autónoma de México, Ciudad Universitaria, Coyoacán, 04510, México D.F., Mexico

Facultad de Estudios Superiores Cuautitlán, Universidad Nacional Autónoma de México, Cuautitlán Izcalli, C.P. 54700, Estado de, México, Mexico

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### Abstract



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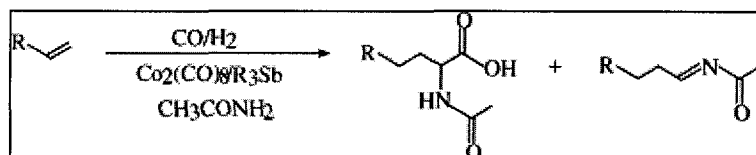
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unsaturated substrates in very mild conditions in the presence of a cobalt–stibine-modified system in comparison to some classical cobalt–phosphine precursors. The stibine and phosphine ligands used were: triphenylstibine (TPS), *o*- and *p*-tritolylstibine (*o*-TTS, *p*-TTS), phenyl(phenylethynyl)mesitylstibine (PPEMS), phenylthienylmesitylstibine (PTMS), *p*-fluorophenylstibine (*p*-TFPS), triphenylphosphine (TPP), *o*- and *p*-tritolylphosphine (*o*-TTP, *p*-TTP).

Abstract; Graphical Abstract;

## Graphical Abstract

Amidocarbonylation reaction catalysed by a  $\text{Co}_2(\text{CO})_8/\text{SbR}_3$  system was carried out to obtain *N*-acetyl- $\alpha$ -aminoacids from several alkenes. The use of  $\text{R}_3\text{Sb}$  ligands not only enhances the catalytic activity but also increases the selectivity at very low pressures.



Full-size image (2K)

**Author Keywords:** Author Keywords: Wakamatsu reaction; Amidocarbonylation; Homogeneous catalysis; *N*-acetyl- $\alpha$ -aminoacid; Cobalt–stibine catalyst

## Article Outline

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